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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : <b>B01J 31/00, 37/00, C08F 4/02, 4/60</b></p>		<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 99/03580</b> (43) International Publication Date: 28 January 1999 (28.01.99)</p>
<p>(21) International Application Number: <b>PCT/US98/13690</b> (22) International Filing Date: 1 July 1998 (01.07.98)</p>		<p>(81) Designated States: AU, CA, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p>	
<p>(30) Priority Data: 08/892,592 14 July 1997 (14.07.97) US</p>		<p><b>Published</b> <i>With international search report.</i></p>	
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<p>(54) Title: PREPARATION OF SUPPORTED CATALYST USING TRIALKYLALUMINUM-METALLOCENE CONTACT PRODUCTS</p>			
<p>(57) Abstract</p> <p>A silica-supported metallocene catalyst made from two components is disclosed. The first component is made from dried silica having hydroxyl groups and an alumoxane scurried together and then dried of its solvent. The second component is made by contacting a group 4 metallocene and a trialkylaluminum in a solvent in which the metallocene is insoluble. The two components are then combined to form the metallocene catalyst.</p>			

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PREPARATION OF SUPPORTED CATALYST USING TRIALKYLALUMINUM-METALLOCENE CONTACT PRODUCTS

The invention relates to new catalyst compositions. In particular, the invention relates to supported metallocene catalysts and new methods of their synthesis.

Metallocene catalysts, activated by alumoxanes, were introduced to the art of catalysis in the late 1970s. The efforts to maximize their efficacy have led to various 5 unique developments. Because of the initial problems involving alumoxanes, some of the developments involved different techniques for producing the cocatalyst (or activator) and to alternatives of activating metallocene complexes.

The invention relates to a supported (heterogeneous) catalyst. The catalyst takes the form of particles which are free flowing and comprise a fully activated, 10 single-component metallocene catalyst.

The supported catalyst is a contact product comprising components (A) and (B). Component (A) is the contact product of silica containing hydroxyl groups and aluminoxane. The molar ratio of hydroxyl groups on the silica surface to aluminum provided by aluminoxane ranges from 0.01 to 1.50. Component (B) is the contact 15 product of a metallocene compound of transition metal and a trialkylaluminum compound; the contact product of (B) is soluble in a paraffinic hydrocarbon containing at least 5 carbon atoms. The transition metal compound has the formula  $Cp_xMA_yB_z$ , wherein Cp is a cyclopentadienyl group, unsubstituted or substituted, x is 1 or 2; M is zirconium, hafnium, or titanium; each of A and B is selected from the group 20 consisting of a halogen atom, a hydrogen atom, and an alkyl group, providing that  $x+y+z$  is equal to the valence of the M; the trialkylaluminum compound in the contact product (B) is characterized by the formula  $Al(M)_a(N)_b(P)_c$  wherein each of M, N, and P is a straight-chain or branched alkyl group containing 1 to 10 carbon atoms, wherein M, N, and P are the same or different, and wherein the sum of  $a+b+c$  is equal to 3. 25 The metallocene transition metal compound per se is not very soluble in said paraffinic hydrocarbon and the transition metal compound derivatives affixed to said support are not soluble in the paraffinic hydrocarbon.

The invention also comprises a process for preparing a catalyst composition comprising providing silica which has been dehydrated at temperatures ranging from

200° to 750°C; contacting said silica with an amount of alumoxane; impregnating the contact product with a solution of an intermediate which has been formed by contacting a metallocene compound of a transition metal with a trialkylaluminum compound in a paraffinic hydrocarbon which is a solvent for the intermediate and in which the transition metal compound itself is not very soluble, wherein the transition metal compound has the formula  $Cp_xMA_yB_z$  in which the  $Cp$ ,  $x$ ,  $M$ ,  $A$ ,  $B$   $x+y+z$  are defined as above; and recovering a supported catalyst in which  $M$  and derivatives thereof are fixed to the silica and are insoluble in said hydrocarbon.

The catalyst of the invention is a supported (heterogeneous) catalyst and comprises 0.05 to 2.00 weight percent (wt.-%), preferably 0.10 to 0.60 wt.% of a transition metal provided by a metallocene compound of a transition metal of the formula  $Cp_xMA_yB_z$ . The catalyst comprises two sources of aluminum. It is characterized by a total aluminum content of 5 to 20 wt.-%, preferably 8 to 15 wt.% of aluminum which refers to the total aluminum content provided by both a trialkylaluminum compound and an alumoxane. (The foregoing weight percents are based on the combined weight of support and metals).

The catalyst comprises a contact product, and derivatives thereof, of an alumoxane and the support, silica or silica/alumina, or alumina. The catalyst composition of the invention can be characterized as the contact product of components (A) and (B), wherein:

component (A) is the contact product of a support, such as silica containing hydroxyl groups, and an alumoxane; and,

component (B) is the contact product of a metallocene compound of a transition metal and an alkylaluminum compound such as a trialkylaluminum compound.

The support for the catalyst may be any carrier material which contains surface hydroxyl groups.

The preferred carrier material for the catalyst is a solid, particulate, porous, inorganic material, such as an oxide of silicon and/or of aluminum. The carrier material is used in the form of a dry powder having an average particle size of from 1 micron to 500 microns. The surface area of the carrier is at least 3  $m^2/g$ , and

preferably from at least 50 m<sup>2</sup>/g up to 350 m<sup>2</sup>/g. The carrier material should be dry, that is, free of absorbed water. Drying of the carrier material can be effected by heating at 100°C to 1000°C. When the carrier is silica, it is heated to at least 200°C, preferably 200°C to 850°C, and most preferably at 600°C. The number of hydroxyl groups (silanol groups in the case of silica) is inversely proportional to the 5 temperature of dehydration: the higher the temperature the lower the hydroxyl content. The carrier material must have at least some active hydroxyl (OH) groups on its surface to produce the catalyst composition of this invention.

In the most preferred embodiment, the carrier is silica which, prior to the use 10 thereof in the first catalyst synthesis step, has been dehydrated by fluidizing it with nitrogen and heating at 600°C for 4-16 hours to achieve a surface hydroxyl group concentration of 0.7 millimoles per gram (mmol/g). The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area = 300 m<sup>2</sup>/g; pore volume of 1.65 cm<sup>3</sup>/g), and it is a material marketed under the tradenames of Davison 15 952 or Davison 955 by the Davison Chemical Division of W. R. Grace and Company or Crosfield ES70 by Crosfield Limited. The silica is in the form of spherical particles, which are obtained by a spray-drying process. As procured, these silicas are not calcined and thus must be dehydrated as indicated above.

Alumoxane is a class of oligomers which includes methylalumoxane. 20 Methylalumoxane (MAO) is used as a cocatalyst with metallocene catalysts. The class of alumoxanes comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula: R-(Al(R)-O)<sub>n</sub>-AlR<sub>2</sub> for oligomeric, linear alumoxanes and (-Al(R)-O-)<sub>m</sub> for oligomeric cyclic alumoxanes wherein n is 1-40, preferably 10-20, m 25 is 3-40, preferably 3-20 and R is a C<sub>1</sub>-C<sub>8</sub> alkyl group or mixtures thereof, preferably a methyl group. MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of 1200. MAO is commonly produced by reacting trimethylaluminum with water or with hydrated inorganic salts. MAO is a solid and is typically kept in solution in toluene.

Contact of the alumoxane with the support results in a reaction product of the 30 alumoxane and the support. When the support is silica, the contact product, which can be termed an aluminosilicate, is formed. The reaction between the support and

the alumoxane occurs via hydroxyl groups of the support; thus, if the support is silica, the reaction occurs via silanol groups. Confirmation of the formation of this unique product resides in two additional independent sources of evidence. First, after contact with the support, the alumoxane cannot be extracted off of the support with toluene. Second, NMR [nuclear magnetic resonance] spectrum of the product shows that a signal unique to alumoxane per se disappears after the support is contacted with the alumoxane.

Contact of the support with alumoxane is undertaken at a -10°C to 80°C temperature range and at ambient pressure. The contact can be undertaken in several steps. The amount of alumoxane relative to a support is controlled by the available hydroxyl groups on the support or by the amount of deposition of alumoxane required. Typically, the amount of alumoxane is 2-10 mmol/g support, preferably 4 to 8 mmol/g support. This catalyst synthesis step is undertaken under inert conditions, in the absence of water and oxygen.

In one embodiment of the invention, the support is contacted with a solution of the alumoxane provided as a volume which is equal to the pore volume of the support, so that no slurry of the support is formed during the alumoxane/support contact step. Although the presently preferred solvent is toluene, it can also be another aromatic hydrocarbon or an aliphatic hydrocarbon.

In a second embodiment of contacting the support with alumoxane, the support is used as a slurry in a paraffinic hydrocarbon. In the slurry embodiment of making the alumoxane/support contact product, a solvent system is used which effects the contact and allows the reaction of the support and an alumoxane. In this second embodiment of alumoxane/support contact, the total volume of the liquid medium is greater than the pore volume of the support. The solvent may be a straight-chain or branched alkane containing 5 to 15 carbon atoms selected from the group of isohexane, hexane, heptane or isopentane. The support is dispersed therein to form a slurry. The total solvent system in this case may include one hydrocarbon solvent of 5 to 15 carbon atoms or at least two hydrocarbon solvents; in the latter instance, the solvents may be miscible and one of them may constitute a solvent for the alumoxane, while the second solvent may be a non-solvent for the

alumoxane. Solvents for the alumoxane include aromatic and aliphatic hydrocarbons, preferably toluene. All solvents should be purified, such as by percolation through silica gel and/or molecular sieves to remove traces of water, oxygen, polar compounds, and other materials capable of adversely affecting catalyst activity.

5 No isolation of the contact product (A) of a support and an alumoxane is required for depositing or impregnating the transition metal derivative into the contact product. However, isolation of the support-alumoxane contact product (A) is also possible. In the embodiments given below, the transition metal complex is added directly to the support-alumoxane contact product (A), in situ.

10 The transition-metal metallocene complex is deposited or impregnated into the contact product (A) as a contact product (B) of an alkylaluminum compound and the metallocene complex. Deposition or impregnation of the contact product (A) of a support and an alumoxane with the contact product (B) comprising a transition metal derivative results in the formation of a new contact product; this statement includes a 15 possibility of a chemical reaction between the support-alumoxane contact product (A) and the transition-metal metallocene complex.

20 The transition-metal metallocene compound has the formula  $Cp_xMA_yB_z$ . This metallocene compound is preliminarily contacted with an alkylaluminum compound, preferably a trialkylaluminum compound. Metallocene compounds, although not very soluble in paraffins, can be readily dissolved in them in the presence of a trialkylaluminum compound. The dissolved transition metal compound is believed to be a unique chemical entity as metallocene compounds, absent the alkylaluminum, are not very soluble in hydrocarbon solvents. The alkylaluminum compound: 25 metallocene ratios correspond to molar ratios of 1 to 100, preferably 5 to 50. Furthermore, the molar ratio of the aluminum, provided by the alumoxane, to the transition metal in the metallocene complex ranges from 50 to 500, preferably 100 to 300. Contact of these two components, a metallocene complex and a trialkylaluminum compound, is undertaken in a paraffinic hydrocarbon solvent such as straight-chain or branched alkanes containing at least 5 carbon atoms and 30 exemplified by pentane, isopentane, hexane, isohexane, n-heptane, and isoheptane.

The alkylaluminum compound, preferably a trialkylaluminum compound, which is contacted with the metallocene compound, is characterized by the formula Al([M]<sub>a</sub>)([N]<sub>b</sub>)([P]<sub>c</sub>), wherein each of M, N, and P is an alkyl group, (straight-chain or branched), or a halogen atom, but is preferably an alkyl group containing 1 to 10 5 carbon atoms; and each of M, N, and P is the same or different. The alkyl groups can be methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, isopentyl, hexyl, isohexyl, heptyl, isoheptyl, octyl, or isoocetyl. Most preferably, this component is trimethylaluminum (TMA). The alkylaluminum compound, preferably trialkylaluminum compound, is contacted with the metallocene compound in the absence of 10 alumoxane. This statement means that any product realized by the contact of the metallocene compound and a trialkylaluminum compound does not involve water and/or an alumoxane.

The metallocene compound has the formula Cp<sub>x</sub>MA<sub>y</sub>B<sub>z</sub> in which Cp is an unsubstituted or substituted cyclopentadienyl group, M is a zirconium, hafnium or 15 titanium atom and A and B belong to the group including a halogen atom, a hydrogen atom or an alkyl group. In the above formula of the metallocene compound, the preferred transition metal atom M is zirconium. In the above formula of the metallocene compound, the Cp group is an unsubstituted, a mono-, a di-substituted, a tri-substituted or a polysubstituted cyclopentadienyl group: and x is at least 1 and 20 preferably is 2. The substituents on the cyclopentadienyl group can be preferably straight-chain C<sub>1</sub>-C<sub>6</sub> alkyl groups. The cyclopentadienyl group can also be a part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated indenyl or fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when x in the above formula of the metallocene 25 compound is equal to 2, the cyclopentadienyl groups can be also bridged by polymethylene or dialkylsilane groups, such as -CH<sub>2</sub>- , -CH<sub>2</sub>-CH<sub>2</sub> , -CR'R"- and -CR'R"- CR'R"- where R' and R" are short chain alkyl groups or hydrogen atoms, -Si(CH<sub>3</sub>)<sub>2</sub>- , -Si(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>2</sub>- , and similar bridge groups. If the A and B substituents in 30 the above formula of the metallocene compound are halogen atoms, they belong to the group of fluorine, chlorine, bromine or iodine; and y + z is 3 or less, provided that x + y + z equals the valence of M. If the substituents A and B in the above formula of

the metallocene compound are alkyl groups, they are preferably straight-chain or branched C<sub>1</sub>-C<sub>8</sub> alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl.

Suitable metallocene compounds include:

- 5    bis(cyclopentadienyl)metal dihalides,
- bis(cyclopentadienyl)metal hydridohalides,
- bis(cyclopentadienyl)metal monoalkyl monohalides,
- bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal dihalides wherein the metal is a zirconium, hafnium or titanium atom; halide groups are preferably chlorine atoms
- 10    and the alkyl groups are C<sub>1</sub>-C<sub>8</sub> alkyls. Illustrative but non-limiting examples of metallocenes include:
- bis(cyclopentadienyl)zirconium dichloride,
- bis(cyclopentadienyl)hafnium dichloride,
- bis(cyclopentadienyl)titanium dichloride,
- 15    bis(cyclopentadienyl)zirconium dimethyl,
- bis(cyclopentadienyl)hafnium dimethyl,
- bis(cyclopentadienyl)zirconium hydridochloride,
- bis(cyclopentadienyl)hafnium hydridochloride,
- bis(n-butylcyclopentadienyl)zirconium dichloride { $(n\text{-BuCp}_2\text{ZrCl}_2)$ },
- 20    bis(n-butylcyclopentadienyl)hafnium dichloride,
- bis(n-butylcyclopentadienyl)zirconium dimethyl,
- bis(n-butylcyclopentadienyl)hafnium dimethyl,
- bis(n-butylcyclopentadienyl)zirconium hydridochloride,
- bis(n-butylcyclopentadienyl)hafnium hydridochloride,
- 25    bis(1,3-dimethylcyclopentadienyl)zirconium dichloride,
- ethylenebis(1-indenyl)zirconium dichloride,
- bis(pentamethylcyclopentadienyl)hafnium dichloride,
- cyclopentadienylzirconium trichloride,
- bis(indenyl)zirconium dichloride,
- 30    bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and
- ethylene[bis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride.

As an example, the contact product (B) of the invention may be prepared using (n-BuCp)<sub>2</sub>ZrCl<sub>2</sub> and TMA.

After mixing contact products (A) and (B), to form the final contact product, excess solvent is removed by evaporation at an elevated temperature. In the 5 process, the soluble metallocene-containing contact product (B) becomes affixed to the contact product (A). It is thereafter insoluble in same solvent system which was used to prepare the final contact product. Preferably the drying temperature is below 90°C and more preferably it is below 60°C.

The dried catalyst of this invention exists in a particulate form. It can be fed to 10 a gas-phase fluidized-bed reactor or to a slurry reactor for polymerization and copolymerization of ethylene in the absence of an additional alumoxane.

The temperature of polymerization can range from 25° to 125°C, but more generally between 50° and 115°C, at pressures of less than 1000 psi.

The catalyst can be used to produce high density polyethylene but it is most 15 commercially valuable for the production of linear low density polyethylene (LLDPE) resins in a particulate form. The LLDPE copolymers of ethylene and 1-olefins contain at least 80 wt.% ethylene and less than 20 wt.% of an alpha-olefin of 3 to 10 carbon atoms, preferably of 4 to 10 carbon atoms, including propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, and 1-octene. These LLDPE products exhibit MFR 20 values [ $I_{21.6}/I_{2.16}$  ratios, each of which is measured according to ASTM D-1238, Conditions F and E] of less than 25.

#### Example 1

Into a three-necked flask was added Davison-grade 955 silica (2.50 g) which 25 was previously calcined at 600°C for 4 hours. The dry silica bed was stirred and, at ambient temperature, methalumoxane (MAO) solution in toluene (12.50 mmol, 3 ml) was added to it in a period of 12 minutes. The liquid was completely absorbed inside the silica pores. After stirring the solid bed for 40 minutes, isohexane (100 ml) was added to it and the slurry was stirred for 25 minutes. Separately, a heptane solution 30 of a zirconocene complex was prepared by reacting trimethylaluminum (TMA) (2.50 mmol) in heptane solution (2 ml) with (n-BuCp)<sub>2</sub>ZrCl<sub>2</sub> (0.0625 mmol, 0.0253 g). This solution was added to the above silica-MAO slurry at an ambient temperature. After

stirring the mixture at ambient temperature for 45 minutes, the solvents were removed by evaporation at 50°C under a nitrogen flow to yield a pale-yellow, free-flowing powder.

Example 2

5        Into a three-necked flask was added Davison-grade 955 silica (2.50 g) which was previously calcined at 600°C for 4 hours, followed by isohexane (100 ml). To this stirred slurry at ambient temperature was added MAO solution in toluene (12.50 mmol, 3 ml). The mixture was stirred for 80 minutes at ambient temperature. Separately, a heptane solution of a zirconocene complex was prepared by reacting  
10      TMA (2.50 mmol) in heptane solution (2 ml) with (n-BuCp<sub>2</sub>)ZrCl<sub>2</sub> (0.0625 mmol, 0.0253 g). This solution was added to the above silica-MAO mixture at ambient temperature. After stirring the mixture at ambient temperature for 45 minutes, the solvents were removed by evaporation at 50°C under a nitrogen flow to yield a pale-yellow, free-flowing powder.

15      Example 3

      Into a three-necked flask was added Davison-grade 955 silica (2.50 g) which was previously calcined at 600°C for 4 hours. To this stirred silica bed at ambient temperature was added MAO solution in toluene (12.50 mmol, 3 ml) in a period of 6 minutes. The liquid was completely absorbed inside the silica pores. The solid bed  
20      was stirred for 120 minutes. Separately, a heptane solution of a zirconocene complex was prepared by reacting TMA (2.50 mmol) in heptane solution (2 ml) with (n-BuCp<sub>2</sub>)ZrCl<sub>2</sub> (0.0625 mmol, 0.0253 g). This solution was added to the above solid silica-MAO bed at an ambient temperature in a period of 6 minutes. All the heptane solution was absorbed inside the silica pores. After stirring the mixture at ambient  
25      temperature for 30 minutes, it was heated at 50°C under a nitrogen flow to yield a pale-yellow, free-flowing powder.

Example 4

      Same as Example 2 except 17.50 mmol MAO and 0.0875 mmol (0.0354 g) of (n-BuCp<sub>2</sub>)ZrCl<sub>2</sub> were used.

Slurry Polymerization Reactions

Ethylene/1-hexene copolymers were prepared using catalysts of Examples 1-4 and an additional amount of a trialkylaluminum compound as an impurity scavenger. An example is given below.

5 A 1.6-liter stainless-steel autoclave equipped with a magnet-drive impeller stirrer was filled with heptane (750 ml) and 1-hexene (165 ml) under a slow nitrogen purge at 50°C, and then 2.0 mmol of triethylaluminum was added to the reactor. The stirring was increased to 1000 rpm, and the temperature was increased to 75°C. Then ethylene was introduced to maintain the total pressure at 210 psig. Finally,

10 10 35.8 mg of the catalyst of Example 1 was introduced into the reactor with ethylene over-pressure, and the temperature was held at 75°C. The polymerization reaction was carried out for one hour and then the ethylene supply was stopped. The reactor was cooled to an ambient temperature and the polyethylene was collected.

15 The slurry polymerization results are given below:

15	Catalyst	Productivity g/gh	Melt Index	MFR	Mole% hexene in copolymer
20	Example 1	2410	1.18	18.1	1.90
	Example 2	2710	1.18	17.9	2.15
	Example 3	1630	0.54	16.9	1.90
	Example 4	3330	0.91	17.7	2.25

25 The data show that the new catalyst systems are highly active. As described above, the supported catalysts can be prepared either in the presence or in the absence of a saturated hydrocarbon during preparation of contact product (A), although higher productivities are obtained when a saturated hydrocarbon is employed in the preparative scheme (compare Examples 1 and 3 with Examples 2 and 4).

30 Thus it is apparent that there has been provided, in accordance with the invention, a synthesis that fully satisfies the objects, aims, and advantages set forth above. While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives,

modifications, and variations as fall within the spirit and broad scope of the appended claims.

CLAIMS:

1. A single-component contact product for homopolymerization of ethylene and copolymerization of ethylene and alpha-olefins, comprising components (A) and (B), wherein component (A) is the contact product of silica containing hydroxyl groups and an alumoxane,

5 wherein a molar ratio of hydroxyl groups in silica to aluminum in the alumoxane, ranges from 0.01 to 1.50; and component (B) is the contact product of a metallocene compound of a transition metal and a trialkylaluminum compound, wherein the contact product (B) is soluble in paraffinic hydrocarbons containing at least 5 carbon atoms,

10 wherein the metallocene transition metal compound has the formula  $Cp_xMA_yB_z$ , wherein Cp is a cyclopentadienyl group, unsubstituted or substituted, or part of a bicyclic or tricyclic moiety x is 1 or 2, or when x equals 2, the cyclopentadienyl groups can be bridged, M is zirconium, hafnium, or titanium; each of A and B is selected from the group consisting of a halogen atom, a hydrogen atom, and an alkyl group providing that x+y+z is equal to the valence of the M;

15 and wherein the trialkylaluminum compound in the contact product (B) is characterized by the formula  $Al(M)_a(N)_b(P)_c$  wherein each of M, N, and P is a straight-chain or branched alkyl group containing 1 to 10 carbon atoms, wherein M, N, and P are the same or different, and wherein the sum of a+b+c is 3.

20

- 2. The single component contact product of Claim 1, wherein the cyclopentadienyl is a substituted cyclopentadienyl and is substituted by at least one alkyl group containing 1 to 10 carbon atoms.

3. The single component contact product of Claim 1, wherein A and B are the same.

4. The single component contact product of Claim 1, wherein the cyclopentadienyl is provided by a group which is a fused ring containing 9 to 16 carbon atoms.

5. The single component contact product of Claim 4, wherein the group which is a fused ring is indenyl.

6. The single component contact product of Claim 2 wherein the alkyl is selected from the group consisting of methyl, ethyl, propyl, butyl, isobutyl, pentyl and isopentyl.

7. The single component contact product of Claim 6 wherein the x is 2 and Cp is butylcyclopentadienyl.

8. The single component contact product of Claim 7, wherein A and B are chlorine.

9. A process for preparing a catalyst composition comprising providing silica which has been dehydrated at temperatures ranging from 200° to 750°C contacting said silica with an amount of alumoxane; impregnating said silica with a solution of an intermediate which has been formed by 5 contacting a transition metal compound with a trialkylaluminum compound to form a contact product, in a hydrocarbon which is a solvent for the contact product and in which the transition metal compound is insoluble,

wherein the transition metal compound has the formula  $Cp_xMA_yB_z$

wherein Cp is cyclopentadienyl unsubstituted or substituted, x is 1 or 2,

10        M is zirconium, hafnium, or titanium; each of A and B is selected from the group consisting of a halogen atom, a hydrogen atom, and an alkyl group providing that  $x+y+z$  is equal to the valence of the M; and wherein the trialkylaluminum provided for the contact product (B) is characterized by the formula  $Al(M)_a(N)_b(P)_c$  wherein each of M, N, and P is a straight-chain or branched alkyl group containing 1 to 10 carbon atoms, wherein M, N, and P are the same or different, and wherein the sum of  $a+b+c$  is 3; and, wherein Al is aluminum and wherein each of M, N and P is the same or different.; and

15        recovering a supported catalyst in which M and derivatives thereof are fixed to the silica and M and its derivatives are insoluble in said hydrocarbon.

20

10.       The process of Claim 9, wherein the transition metal compound is introduced into said hydrocarbon which is a paraffin containing 5 to 15 carbon atoms in which said transition metal compound is insoluble; adding to said hydrocarbon an amount of trimethylaluminum or triethylaluminum, said amount being sufficient to 5 produce a solution.

11.       The process of Claim 10, wherein said hydrocarbon is isopentane, hexane, isohexane, heptane, isoheptane or admixtures thereof.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/13690

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B01J 31/00, 37/00; C08F 4/02, 4/60  
US CL : 502/103, 104, 107, 110, 117, 132

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/103, 104, 107, 110, 117, 132

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,701,432 A (WELBORN, JR.) 20 October 1987, col. 16, lines 15-45.	1-11
Y	US 5,422,325 A (JEJELOWO et al) 06 June 1995, col. 6, lines 32-45.	1-11
Y,P	US 5,703,180 A (TSUTSUI et al) 30 December 1997, col. 32, lines 10-46.	1-11
Y,E	US 5,795,838 A (TSUTSUI et al) 18 August 1998, col. 48, line 44 to col. 49, line 14.	1-11
Y,E	US 5,795,839 A (KATAOKA et al) 18 August 1998, col. 25, table 3, inventive examples 26, 27, 29-31; comparison examples 5 and 6.	1-11

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

27 AUGUST 1998

Date of mailing of the international search report

22 OCT 1998

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